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Stress Corrosion Cracking Damages

Alireza Khalifeh

Abstract

Stress corrosion cracking (SCC) is the formation and growth of crack through materials subjected to tensile stress and a specific corrosive medium. It can lead to unexpected sudden failure of normally ductile metals. Metal-environment combinations susceptible to cracking are specific. This means that all environments do not cause SCC on all of the alloys. Additionally, the environments that cause this kind of cracking have little corrosion effect on the alloy in normal conditions. In certain states, unwanted environmental and metallurgical changes have occurred and provide the metal-environment combination sensitive to SCC. The SCC sites on the metal surfaces may not be visible by visual inspection, while metal parts are being filled with microscopic cracks. These invisible cracks progress rapidly and lead the component and structures to catastrophic failures. In this chapter, the incidence of SCC on important industrial alloys from the chemical, metallurgical, and mechanical point of view is discussed.

Keywords: stress corrosion cracking, environments, materials, mechanisms, fracture mechanic

1. Introduction

Stress corrosion cracking (SCC) in chemical, petrochemical, and power plant industries is an insidious form of corrosion, which causes a lot of financial losses and human damages [1–5]. This phenomenon is associated with a combination of tensile stress, environment, and some metallurgical conditions as described in **Figure 1**.

During stress corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine and branch cracks progress through the bulk of material [6]. It is shown in **Figure 2**. This cracking phenomenon has serious consequences since it can occur under stresses much lower than design stresses and lead the equipment and structures to premature failures [7–11].

Stress corrosion cracking starts from corrosion sites at the material surfaces and progresses into a brittle manner. The process of cracking is not strictly a mechanical process, as the corrosivity of the environment strongly affects the fracture mode. Both intergranular and transgranular stress corrosion cracking are observed. Intergranular cracking proceeds along grain boundaries, while transgranular cracking advances without apparent preference for boundaries [12]. An example of stress corrosion cracking in which the crack has progressed in both intergranular and transgranular paths is shown in **Figure 3**. The development mode of cracking depends on the composition and microstructure of the material and environment.

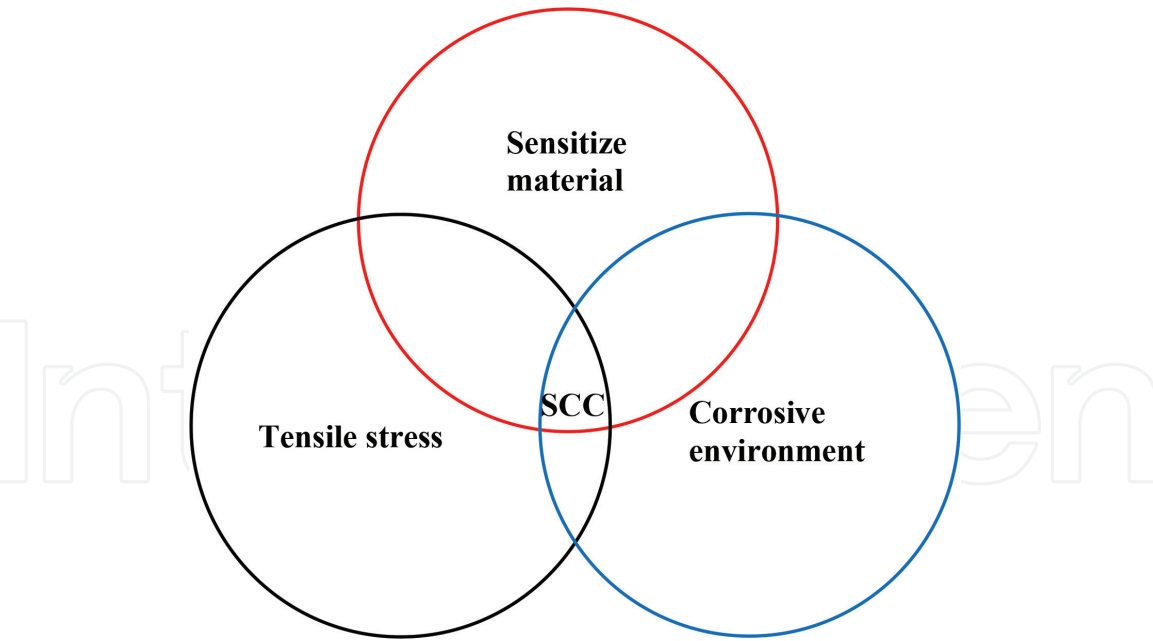


Figure 1.
The essential requirements for SCC.

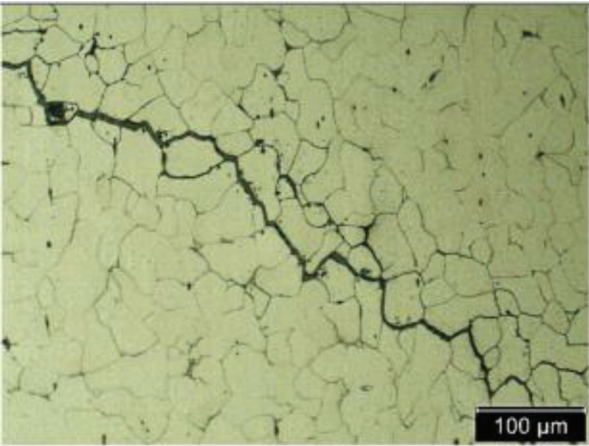


Figure 2.
Crack development in carbon steel exposed to nitrate solution.

In this chapter, the conditions for the occurrence of SCC are first introduced. Then, the stress corrosion cracking mechanism for various materials in conditions that are susceptible is discussed in detail. The design of industrial structures and components is usually based on tensile properties, which have many disadvantages. So, the science of fracture mechanics applies in the situations prone to SCC because of the inevitability of manufacturing and service defects in materials and for considering the role of such imperfections. Methods of prevention based on corrosion science and empirical data are presented. Finally, practical examples are given to better understand the issue.

2. Requirements for SCC

Not all metal-environment combinations are susceptible to cracking. In other words, the environment for occurrences of SCC for each metal or alloys is specific. Also, the resources of stress for each case of failure may be different.

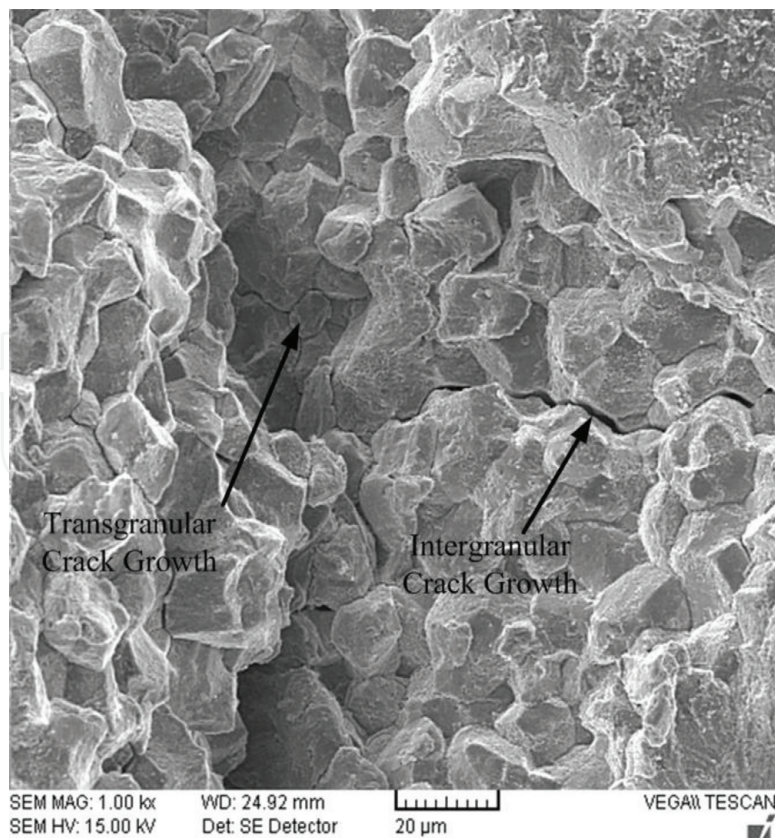


Figure 3.
Intergranular and transgranular stress corrosion cracking of the AISI 316L stainless steel at polythionic acid environment [8].

2.1 Materials

2.1.1 Stainless steels

Austenitic stainless steels suffer from SCC in chlorides, caustic, and polythionic acid. When austenitic stainless steels with sufficient carbon content (more than 0.03 wt.%) are heated in the range of 415–850°C, their microstructure becomes susceptible to precipitation of chromium carbides ($M_{23}C_6$) along grain boundaries known as sensitization [9, 12, 13]. Formation of Cr-rich carbides along grain boundaries may drastically deplete free chromium content in the area adjacent to the grain boundaries and render them susceptible to rapid preferential dissolution. Sensitized steels are most susceptible; the stress corrosion cracking of nonsensitized steels is also observed [14, 15]. Dissolution of grain boundaries in some corrosive environments aside from tensile stress led these types of materials to SCC.

2.1.2 Copper and copper alloys

Seasonal cracking of brass in the rainy season in an ammoniacal environment is another classical example of SCC. This was first identified on the brass cartridge used by the British Army in India. Since it is usually identified during the rainy season, it is also called seasonal cracking [12]. Alpha brass is an alloy of Cu-Zn. It can crack either intergranularly or transgranularly in nontarnishing ammonia solutions, depending on its zinc content [16–18]. Transgranular stress corrosion cracking, TGSCC, is observed in alloys with 20 or 30% Zn but not in alloys with 0.5 or 10% Zn [19, 20]. Stress corrosion cracking of Cu-Zn and Cu-Al alloys in cuprous ammonia solutions can only occur when the parting limits for dealloying are

exceeded. The parting limits are about 14 and 18 a/o for Cu-Al and Cu-Zn, respectively [21]. Cu-Al and Cu-Ga alloys have shown similar behaviors [19, 22].

2.1.3 Aluminum and aluminum alloys

Aluminum and all its alloys can fail by cracking along grain boundaries when simultaneously exposed to specific environments and stresses of sufficient magnitude [23, 24]. Of eight series of aluminum alloys, 2xxx, 5xxx, and 7xxx aluminum alloys are susceptible to SCC. Among them, 7xxx series aluminum alloys have a specific application in aerospace, military, and structural industries due to superior mechanical properties. In these high-strength 7xxx aluminum alloys, SCC plays a vital factor of consideration, as these failures are catastrophic during the service [25].

2.1.4 Carbon steels

Carbon and low alloy steels have shown SCC in a wide range of environments that tend to form a protective passive or oxide film [26–30]. The environments that would passivate carbon steels have been found to cause SCC, including strong caustic solutions, phosphates, nitrates, carbonates, ethanol, and high-temperature water. The problems are important for both economic and safety reasons, due to the extensive use of carbon steels [31]. For example, nitrate cracking in an ammonium nitrate plant caused by catastrophic failures and a lot of financial losses. Caustic cracking of steam-generating boilers made of low alloy steels was a serious problem, which led an ammonia plant to repeated emergency shutdowns.

2.1.5 Titanium alloys

Stress corrosion cracking may be a problem whenever certain high-strength titanium alloys are exposed to aqueous and certain solvent environments [32–36]. For the first time, SCC of titanium was reported by Kiefer and Harple who describe the cracking phenomena with commercially pure titanium in red fuming nitric acid [37]. Hot salt cracking of titanium alloys was reported in turbine blades that operate at high temperature in the mid-1950s. The subject became very active in the early 1960s because of the SCC problem connected to these alloys in a transportation program [38]. The first known report of stress corrosion cracking of titanium alloys in room temperature aqueous environments was that of Brown. He found that titanium alloys, 8% aluminum–1% molybdenum–1% vanadium alloy (Ti, 8–1–1), were susceptible to SCC in seawater [38].

2.2 Environments

Another requirement for SCC to occur is a corrosive environment. The environments for SCC are specific because not all environments promote SCC. For those alloys that develop a protective film, an aggressive ion is required to promote SCC. The aggressive media to passive layer of stainless steels are chlorides, caustic, and polythionic acid. The austenitic stainless steel series 300 is more susceptible in an environment containing chlorides. Chlorides will not cause SCC unless an aqueous phase is present. It appears that stress corrosion cracking in austenitic stainless steels in the presence of chlorides proceeds transgranularly and usually occurs at temperature above 70°C [39, 40]. Cases of SCC due to chlorides have been experienced at ambient temperatures on parts that were subjected to heavy machining [41, 42]. Caustic embrittlement or stress corrosion cracking in caustic environment is another serious problem in austenitic stainless steels and causes many explosions

and other types of failures in steam boiler and super heater components [9, 43–45]. Caustic cracking failures frequently originate in a welding area, which is intergranular, and a very concentrated caustic solution is usually necessary [40]. Polythionic acid is another environment, which causes SCC in austenitic stainless steels. Sulfur in feed gas in chemical and petrochemical plants led to formation of polythionic acid ($H_2S_xO_6$, $x = 2-5$), which aside from moisture also induced intergranular stress corrosion cracking in austenitic stainless steels [46, 47]. Well-known specific environments for the stress corrosion cracking in Al alloys include water vapor, aqueous solutions, organic liquids, and liquid metals [48]. The SCC of Ti alloys in aqueous chloride and methanolic chloride environments at ambient temperatures has been widely reported [49]. The summary of environments that cause SCC in mostly used alloys is presented in **Table 1**.

2.3 Stress

The stress in the form of tensile (not compressive) plays a key role in the SCC fracture processes. In fact, SCC would never have occurred in the absence of stress. The required tensile stresses may be in the form of directly applied stresses, thermal, in the form of residual stresses, or a combination of all [8, 50]:

$$\sigma = \sigma_{\text{applied}} + \sigma_{\text{thermal}} + \sigma_{\text{residual}} \quad (1)$$

For SCC to occur alone by applied stress, it must have a very high magnitude. The welding and mechanical residual stresses are the main sources of stress attributed to the stress corrosion cracking. The welding residual stress is produced as a result of nonuniform temperature changes during welding operation and can be calculated from thermal strain vectors.

The thermal strain vector, $\Delta\epsilon^{th}$, is formulated by a temperature-dependent differential expansion coefficient ($^{\circ}/c$) as follows [2]:

$$\{\Delta\epsilon^{th}\} = [\alpha]\Delta T \quad (2)$$

in which $\Delta\epsilon^{th}$ is the variation of strain, α is the thermal expansion of material, and ΔT is the temperature change.

The operational thermal stress can also be calculated from Eq. 2. Mechanical workings such as cold deformation and forming, machining, and grinding are the other sources, which introduce residual stresses [8, 51].

3. Stress corrosion cracking mechanism

Extensive investigations have been devoted to find mechanisms of SCC for different materials and environments. An SCC failure illustrates the combined effects of mechanical, physical, and chemical/electrochemical factors causing the separation of metal bonds at the crack tip, thereby advancing the crack. Three mechanisms for SCC have been proposed through the investigations [52]:

3.1 Pre-existing active path mechanism

This model supposes that there are pre-existing paths in an alloy that is susceptible to anodic dissolution. Because of precipitation or solute segregation of impurities like sulfur, phosphorus, and chromium carbides, the electrochemical properties of the matrix and segregates are changed. The area adjacent to the grain boundaries

Metal	Environment
Al alloys	NaCl-H ₂ O ₂ solutions
	NaCl solutions
	Seawater
Copper alloys	Ammonia vapor and solutions
	Amines
	Water or water vapor
Gold alloys	FeCl ₃ solutions
	Acetic acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	NaCl-Na ₂ CrO ₄ solutions
	Rural and coastal atmospheres
	Seawater
	Distilled water
Nickel	Fused caustic soda
Steels	NaOH solutions
	NaOH-Na ₂ SiO ₄ solutions
	Calcium, ammonium, and sodium nitrite solutions
	Mixed acids (H ₂ SO ₄ -HNO ₃)
	Acidic H ₂ S solutions
	Seawater
	Carbonate-bicarbonate solutions
Stainless steels	Acidic chloride solutions
	NaCl-H ₂ O ₂ solutions
	Seawater
	H ₂ S
	NaOH-H ₂ S solutions
	Condensing steam from chloride waters
Titanium alloys	Red fuming nitric acid
	Seawater
	Methanol-HCl

Source: Craig and Lane [54].

Table 1.
Summary of some environments caused by SCC on different alloys.

is depleted from one or more alloying elements, and so under such conditions, localized galvanic cells are created (**Figure 4**). Since precipitation or segregation is generally anodic to the matrix of the grains, dissolution under an anodic reaction occurs and provides active path for localized corrosions [53]. Also, the removal of the protective film at the pre-existing crack tips by plastic deformation would facilitate the onset of localized corrosion.

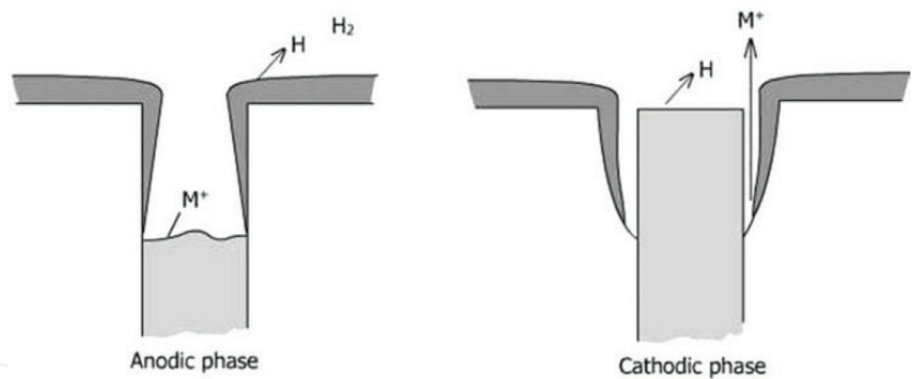


Figure 4.
Galvanic cell mechanism [52].

3.2 Strain-generated active path mechanisms

This mechanism has been extensively studied in stress corrosion cracking of alpha brass in ammoniacal environment and also proposed for caustic cracking of boiler steel. The model is based on the idea of a strain-induced rupture of the protective film, and so plastic strains play a main role in failure processes [52, 55]. The theory assumes the existence of a passivation film on a metal surface. The passivation film protects the underlying metal against corrosive agents. The passivation film is ruptured by plastic strain due to mechanical workings. After the film is ruptured, the bare metal is exposed to the corrosive environment. The processes of disruptive strain (disruption of protective film) and film formation (due to repassivation) have occurred and alternate with each other. The crack propagates when the rate of rupture of oxide film is higher than the rate of repassivation of the film [52]. The mechanism is shown in **Figure 5**.

3.3 Adsorption-related phenomenon

This model is based on the effects of environmental species on interatomic bond strength. The theoretical fracture stress required to separate two layers of atoms of spacing b is given by [56].

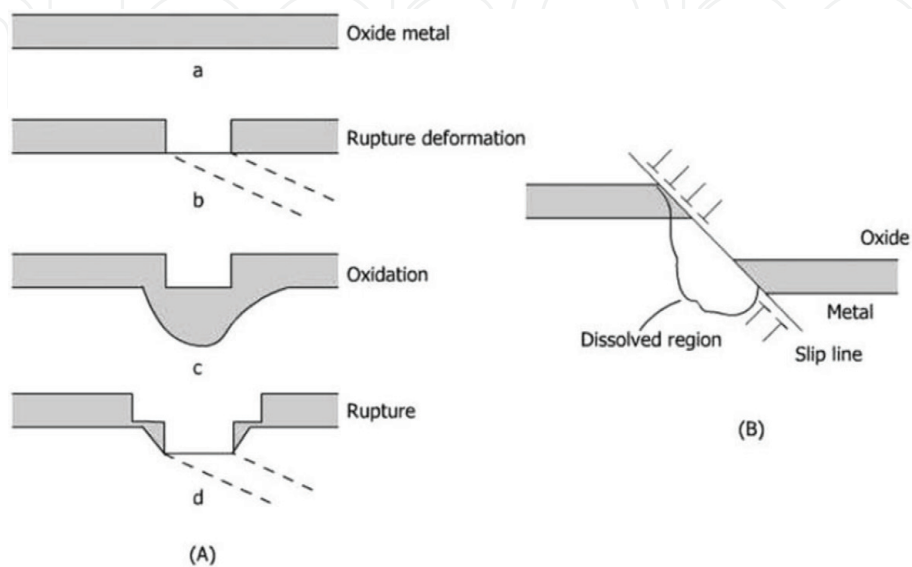


Figure 5.
Strain-generated active path mechanisms. (A) Film rupture model and (B) slip-step dissolution model [52].

$$\sigma_f = \left(\frac{E\gamma_s}{b} \right)^{1/2} \quad (3)$$

where E is the Young modulus, γ is the surface energy, and b is the spacing between atoms.

This theory implies that if surface energy is reduced, then σ_f will also be reduced. In corrosive environments, aggressive agents are present and they are absorbed at the crack tips, the surface energy is effectively lowered, and fracture takes place in stress much lower than design stress [52].

4. Application of fracture mechanics

The design of steel structure and component based on tensile properties has many disadvantages that do not take into account the role of imperfections. Fracture mechanic introduces another material characteristic, namely, fracture toughness, K_{IC} , which considered the role of cracks and imperfection in the form of cracks in designs. In its simplest form [57].

$$K_{IC} = \sigma\sqrt{\pi a} \quad (4)$$

where σ is the design stress and a is the size of an existing crack.

According to this equation, fracture occurs when stress intensity factor, K_I , on the crack tip is equal to K_{IC} . This applies for the propagation of cracks due to mechanical loadings. For the structure parts exposed to corrosive environments, the situation is quietly different. The corrosive agents caused a significant drop in the load capacity and the fracture toughness of the metals. This is typically shown in **Figure 6**. As outlined in the diagram, designs of structures in the corrosive environment based on K_{IC} led the component to failure in a short period of time. Therefore, in these situations, K_{IC} should be replaced with $K_{I_{SCC}}$, which is the threshold value for SCC [12]. This means that in the corrosive environment, the load capacity must be significantly lower than the clean environments. The use of fracture mechanics for high-strength low alloy steels is responsive, but for austenitic steels with branch cracks, the subject should be treated with caution [12].

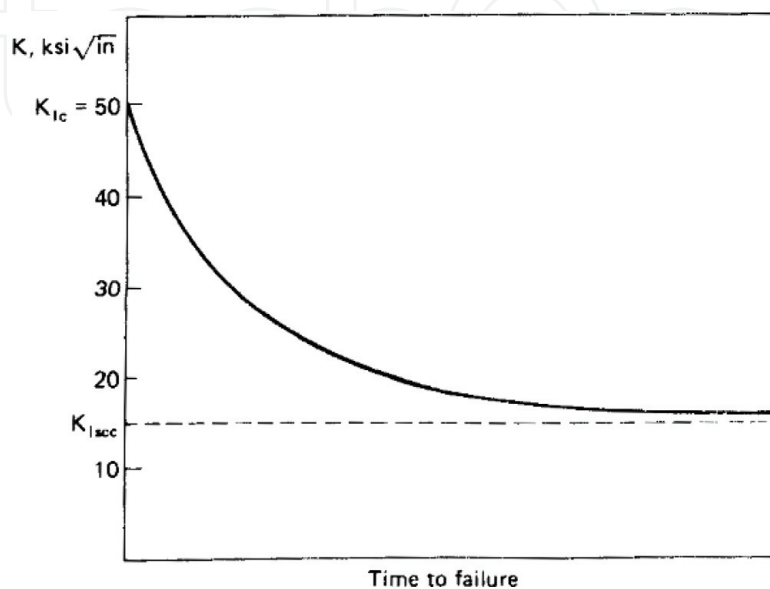


Figure 6.
Effects of corrosive environment on fracture toughness [12].

5. Prevention

Since the exact mechanism of SCC has not been completely understood, prevention methods are either general or empirical in nature. Appropriate strategy should be done in order to minimize this problem to ensure not only the safety of human life but also the safety of cost. The following general methods are recommended to overcome the SCC problems [12, 52, 58, 59]:

- a. Lowering the tensile stress in the welded component using post weld heat treatment. The post weld heat treatment reduced or eliminated residual stress on surface and through the bulk of material. Plain and low alloy steels may be a stress relief at 1100–1200°F. The range of residual stress relief temperature for austenitic stainless steels is from 1500 to 1700°F. Reduction of tensile stresses by shot peening is also recommended. Shot peening introduces surface compressive stresses.
- b. Eliminating aggressive agents from the environment by, for example, degasification, demineralization, or distillation.
- c. Changing the alloy is one possible solution if neither the environment nor stress can be changed. For example, it is a common practice to use Inconel (raising the nickel content) when typical 304 stainless steel is not satisfactory.
- d. Applying cathodic protection: impressed current cathodic protection system has been successfully used to prevent SCC of steels.
- e. Adding inhibitors to the system if feasible: high concentrations of phosphate have been successfully used.
- f. Coatings are sometimes used, and they depend on keeping the environment away from the metal.

6. Failure case studies

6.1 Case 1: stress corrosion cracking of a circulation water heater tube sheet [8]

After only 3 years' service of a circulation water heater (heat exchanger), it has been shown to have severe leakage and has led a methanol plant to emergency shutdown. An on-site investigation revealed extensive cracking initiated at weld area and through the tube sheet holes as it is shown in **Figure 7**.

6.1.1 Material and environment

The circulation water heater is a vertical U-type heat exchanger made of austenitic stainless steels. The equipment used to decline reformed gas temperature in a methanol plant. The hot reformed gas at approximately 385°C entered the tubes and is cooled down to 168°C by exchanging the heat with processed water in the shell. The gases that flow through the tubes are mainly CO₂, CO, H₂, CH₄, and N₂ and at a pressure of 3.9 MPa. At the shell cooling process, water flows with about 6 MPa pressure.

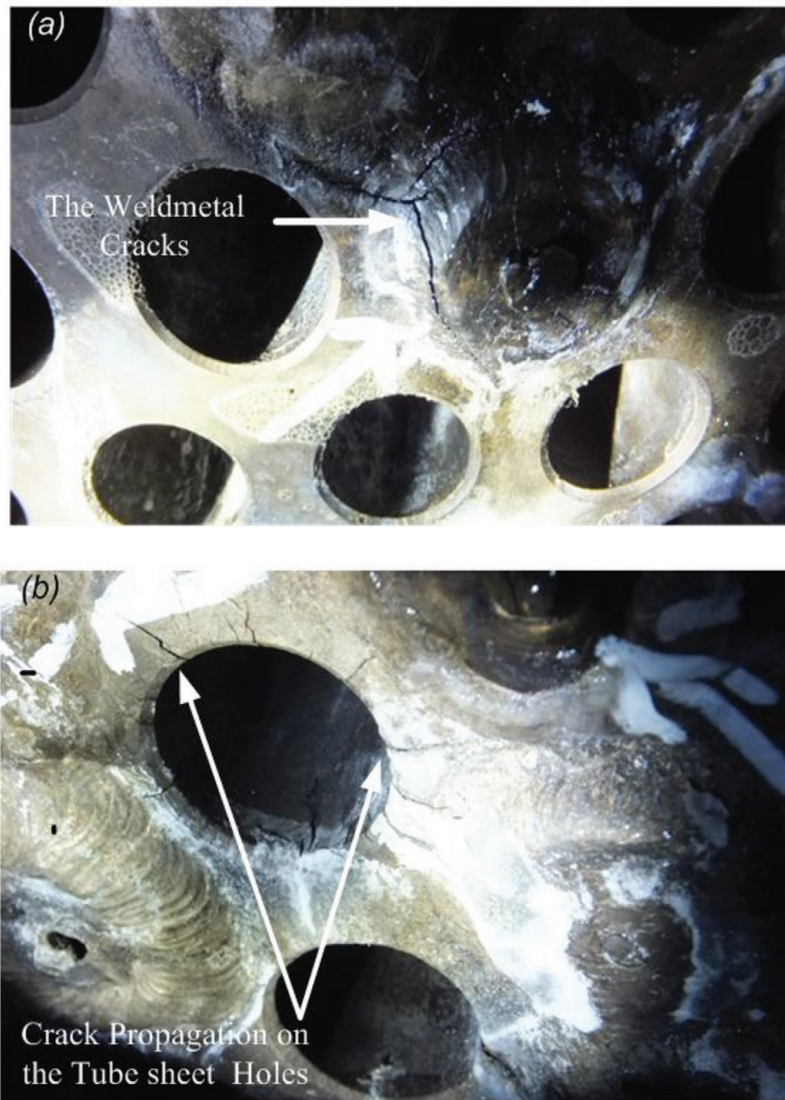


Figure 7.

Failed area (a) cracks extending in the weld joint of tube sheet to plugs and (b) branched cracks in the surface of the tube sheet and through the holes [8].

6.1.2 Cause

Deposits had formed on top of the tube sheet due to shutdown errors. AISI 316L materials overheated in service because of the insulation role of the deposits. Material sensitization occurs since overheating. The presence of sulfur in the process gas aside from moisture formed polythionic acid during shutdowns. Residual stress produced by heavy machining and welding aside from operational thermal stress provided tensile stress, which is needed for SCC. Stress corrosion cracking is induced by polythionic acid. Concentrated water with other aggressive agents such as caustic and chlorides leaked through the cracks aid the failures.

6.1.3 Prevention

- Cleaning of the shell by demineralized water after each shut down in order to prevent the forming of insulating deposits above the tube sheet
- Reduction of sulfur in feeding gas
- Reduction of caustic and chlorides in processed water

6.2 Case 2: failure of an austenitic stainless steel tubes in a gas-fired steam heater [9]

Carryover of caustic soda (NaOH) in the steam path caused catastrophic failure of superheater stainless steel tubes in a gas-fired heater and led to an unexpected shutdown after just 5 months of continuous service following the start of production. The failure areas are shown in **Figure 8**. Three types of cracks are identified in various regions of the tube: circumferential cracks adjacent to the seam weld, circumferential cracks at the ribbon of the seam weld, and longitudinal cracks on the U-bend. The path of cracks was complex on the surface or in the bulk metal; all had nucleated from inside the tubes. A visual inspection revealed a white deposit, high in sodium, around the cracks on the surface of the tubes.

6.2.1 Material and environment

The superheater tube material was made of AISI 304H austenitic stainless steel material.

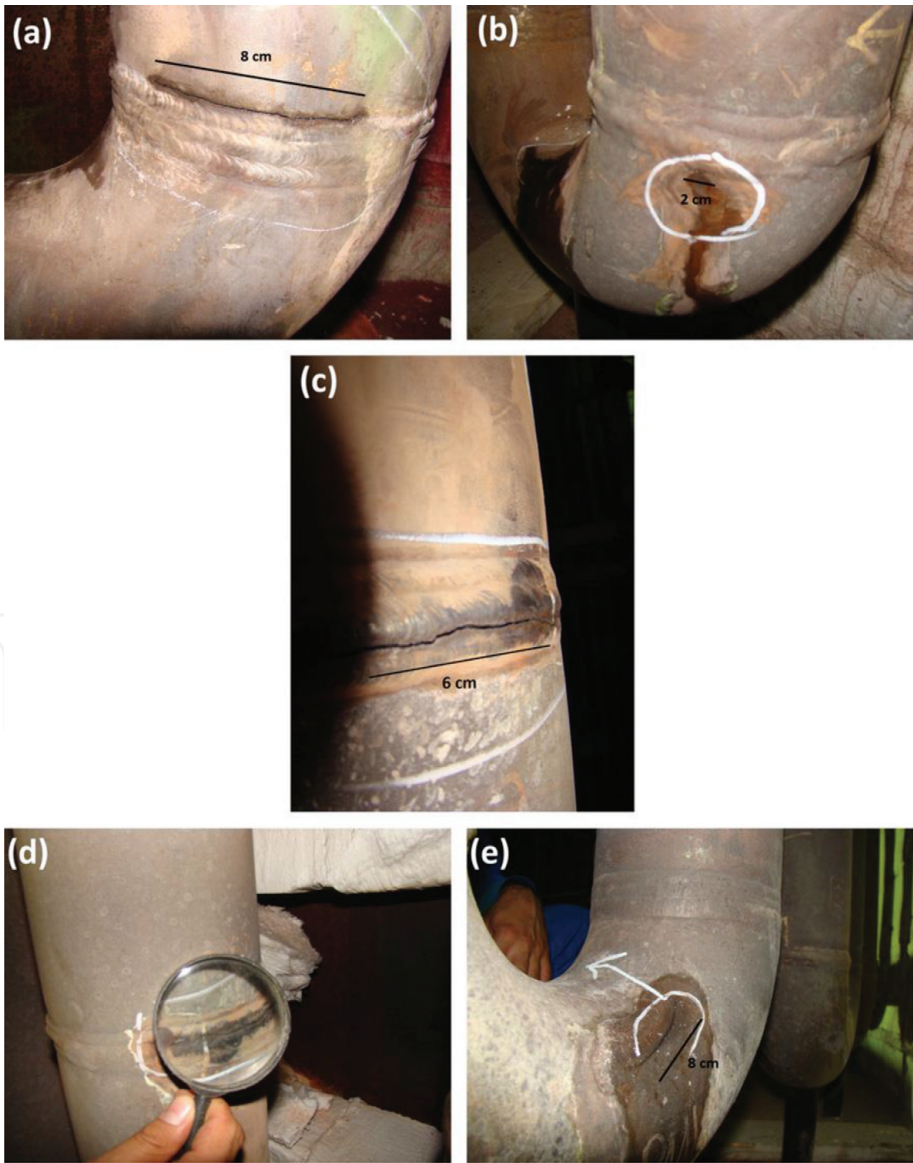


Figure 8.
(a and b) Circumferential cracks adjacent to the seam weld, (c and d) circumferential cracks at the ribbon of seam weld, and (e) longitudinal cracks on the U-bend [9].

The gas-fired steam heater (FH) generates high-pressure (HP) steam for turbines for the processing of methanol. Demineralized water for the boiler and subsequent steam path is prepared in the water treatment unit. Caustic soda is injected to demineralized water for pH control. The water is transferred to the preheat exchangers, is converted to saturated high-pressure steam at 325°C and 119 MPa, and is sent to the FH. Through the FH tubes, saturated steam converted to super-saturate steam at a temperature of 505°C and pressure of 119 MPa.

6.2.2 Cause

The main cause of crack initiation was the increase of pH due to the rise of caustic concentration in condensed drops. Sensitized austenite grains caused by chromium carbide depletion adjacent to the grain boundaries were attacked by concentrated caustic in the HAZ metal and U-bend area and led the heater to the caustic SCC failure.

6.2.3 Prevention

- a. Using A335 Grade P9, a low alloy steel tube shows higher resistance to SCC than AISI 304H stainless steel
- b. Proper discharge of the tubes during shutdowns to prevent the formation of the concentrated deposits of caustic through the tubes

6.3 Case 3: failures of brass condenser tubes [60]

After a general overhaul of a thermal power plant in Serbia in November 2014, failure of hundreds of brass condenser tubes occurred during the hydrostatic test. Also, it was noted that some backing plates had fallen off from the tubes before this test. Fracture is observed only in condenser tubes of brass, as can be seen in **Figure 9**.

6.3.1 Material and environment

The failed tube material of the condenser was made of brass CuZn28Sn1 (admiralty brass). The cooling water (roughly filtered river water) flows through the tubes, while the hot steam flows around the tubes.

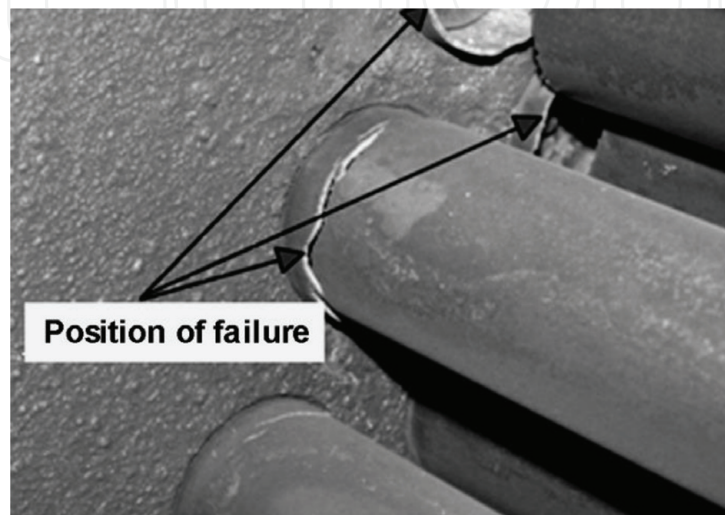


Figure 9.
Failure of brass condenser tubes near joining location with backing plate.

6.3.2 Cause

Analysis of fracture surfaces using scanning electron microscopy (SEM) has shown the brittle transgranular fracture due to the occurrence of SCC. The condenser tubes are made of brass CuZn28Sn1. Ammonia and other nitrogen compounds in the cooling water through the tubes were found. These compounds are specific agents that cause stress corrosion cracking (SCC) in brass. In the joining region of condenser tubes to backing plates, there are residual tensile stresses. During the floods in May 2014, there was an increase in the concentration of ammonia and other nitrogen compounds in the river cooling water flowing through the condenser tubes. Failure of brass condenser tubes occurred due to SCC, because the necessary conditions for the SCC occurrence were fulfilled.

6.3.3 Prevention

- The risk of SCC in brass condenser tubes can be reduced if specific substances responsible for SCC occurrence are removed, as much as possible. This can be achieved by cleaning and drying the tubes immediately after the operation delay of the power plant.
- Another way to reduce the risk of SCC occurrence in condenser tubes is the replacement of existing tubes (made of brass CuZn28Sn1, very susceptible to SCC) with tubes made of alloys of greater resistance to SCC, such as copper-nickel alloys or Bi-brass alloys [61].

7. Conclusion

Stress corrosion cracking is one of the main causes of unforeseen and dangerous destruction of industrial plants. The sensitized material, certain environments, and stress are three factors necessary for the occurrence of these types of failures. The environment prone to the cracking for each metal or alloy is specific because not all environments promote the SCC. Austenitic stainless steels suffer from SCC in chlorides, caustic, and polythionic acid. Copper alloys corrode in ammonia-containing environments. Well-known specific environments for the stress corrosion cracking in Al alloys include water vapor, aqueous solutions, organic liquids, and liquid metals. The SCC of Ti alloys in aqueous chloride and methanolic chloride environments has been widely reported. The tensile stress plays a key role in the stress corrosion cracking phenomenon. The required tensile stresses may be in the form of directly applied stresses, thermal, in the form of residual stresses, or a combination of all.

If one of these three components does not exist, this type of corrosion will not occur. Therefore, the solving methods should be based on the elimination of one of these three factors. Corrosive environment modification, the stress in the form of compression, and using proper material are three general proposed methods of prevention.

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